Seasonal and event variations in δ^{34}S values of stream sulfate in a Vermont forested catchment: Implications for sulfur sources and cycling

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ABSTRACT

Stable sulfur (S) isotope ratios can be used to identify the sources of sulfate contributing to streamwater. We collected weekly and high-flow stream samples for S isotopic analysis of sulfate through the entire water year 2003 plus the snowmelt period of 2004. The study area was the 41-ha forested W-9 catchment at Sleepers River Research Watershed, Vermont, a site known to produce sulfate from weathering of sulfide minerals in the bedrock. The δ^{34}S values of streamwater sulfate followed an annual sinusoidal pattern ranging from about 6.5‰ in early spring to about 10‰ in early fall. During high-flow events, δ^{34}S values typically decreased by 1 to 3‰ from the prevailing seasonal value. The isotopic evidence suggests that stream sulfate concentrations are controlled by: (1) an overall dominance of bedrock-derived sulfate (δ^{34}S ~6–14‰); (2) contributions of pedogenic sulfate (δ^{34}S ~5–6‰) during snowmelt and storms with progressively diminishing contributions during base flow recession; and (3) minor effects of dissimilatory bacterial sulfate reduction and subsequent reoxidation of sulfides. Bedrock should not be overlooked as a source of S in catchment sulfate budgets.

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1. Introduction

Predicting how ecosystems respond to changes in deposition of atmospheric sulfur (S) requires an understanding of sources and cycling of S in the terrestrial landscape. In some watersheds, S inputs and outputs are approximately balanced. Such steady-state conditions, however, do not imply that atmospheric S is simply passing through the landscape. Large reservoirs of S exist in the soil and vegetation, and these pools damp ecosystem responses to changes in S deposition. In other watersheds, S inputs and outputs are not in balance. Net sulfate export may be caused by geologic sources (Alewell et al., 1999; Bailey et al., 2004,

Mitchell et al., 1986; Shanley et al., 2005), net mineralization of organic S (Driscoll et al., 1998; Likens et al., 2002; Park et al., 2003), or net sulfate desorption (Nodvin et al., 1986). Net sulfate retention may be caused by vegetation uptake (Swank et al., 1984), conversion of sulfate to organic S (Mitchell and Alewell, 2007), sulfate adsorption (Rochelle et al., 1987; Shanley and Peters, 1993; Huntington et al., 1994), or dissimilatory bacterial sulfate reduction (Krouse and Mayer, 2000). An ecosystem may be out of steady state with respect to sulfate because it is still adjusting from lower or higher deposition in the past. Isotopic studies have shown that sulfate inputs are strongly retained in the soil and suggest mean residence times of decades (Mayer

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et al., 1995, 2001), implying that ecosystem recovery from declining S deposition will be a gradual process.

In earlier work at Sleepers River, Vermont, we found that sulfate from mineral weathering dominated stream sulfate, but that atmospheric sulfate contributed as much as 50% of stream sulfate during the snowmelt peak (Shanley et al., 2005). However, stream sulfate lacked the distinctively high $\delta^{18}O$ value of atmospheric sulfate, revealing that most atmospheric sulfate was first incorporated in organic matter and subsequently mineralized before entering the stream as pedogenic sulfate. Low recovery in streamwater of cosmogenic ^{35}S (half-life 87 days), which enters the watershed in precipitation, provided independent evidence that the mean residence time of atmospheric S in the watershed was one year or more (Shanley et al., 2005).

In the current study, we extended our sampling for an entire water year, and sampled an additional snowmelt season as well. Our objectives were to answer the following questions:

1. Is bedrock-derived sulfate the dominant source of stream sulfate throughout the year?
2. Are the previously determined sulfate isotope end members during snowmelt valid during the rest of the year?
3. How do inputs of atmospheric/pedogenic sulfate during rain storms affect stream water sulfate compared to those during snowmelt?
4. Is there isotopic evidence of dissimilatory bacterial sulfate reduction?

To this end, we sampled streamwater weekly and collected multiple samples during high-flow events. We limited our spatial sampling to one stream site, based on our earlier finding that the contribution of atmospheric/pedogenic sulfate to streamflow during snowmelt was fairly similar within various sized subcatchments at Sleepers, including both forested and agricultural landscapes (Shanley et al., 2005).

1.1. Site description

Sleepers River W-9 is a 41-ha catchment forested with second-growth Northern Hardwoods dominated by *Acer saccharum* (sugar maple), *Fraxinus americana* (white ash), and *Betula alleghaniensis* (yellow birch), with less than 5% conifer, *Picea rubens* (red spruce) and *Abies balsamea* (balsam fir) (Fig. 1). It was selectively logged in 1929. Elevation ranges from 519 to 671 m. The bedrock is a calcareous phyllite interbedded with sulfidic mica phyllites and biotite schists (Hall, 1959; Bailey et al., 2004). There is up to 3 m of dense basal till with high fine silt content, developed from the local bedrock. Soils are inceptisols, spodosols and histosols developed to 500 to 700 mm depth. The low permeability till supports sustained base flow and gives rise to numerous small wetlands in the hummocky topography. The bedrock and till generate well-buffered Ca-bicarbonate-sulfate streamwater (Shanley et al., 2004). Precipitation is evenly distributed throughout the year and averages 1300 mm with about 25% falling as snow. Spring snowmelt dominates the annual hydrograph, but the peak flow can occur at any time of the year. Mean annual temperature is 4.6 °C.

2. Methods

The study was conducted from September 2002 through October 2003, encompassing Water Year 2003 (which began 1 October 2002), with additional sampling for a few weeks before and during the 2004 snowmelt. During the dormant season (October through May), precipitation and throughfall samples for S isotopic analysis were collected using 1.2-m×1.2-m troughs constructed as a shallow "V" and lined with polyethylene sheeting. The troughs were gently sloped to drain into large polyethylene buckets. The precipitation collector was in a forest clearing and the throughfall collector was
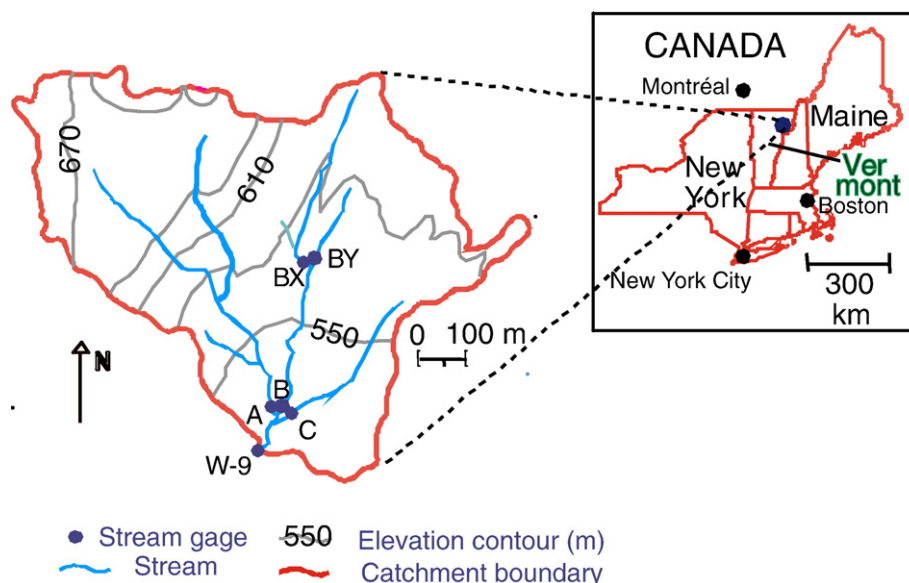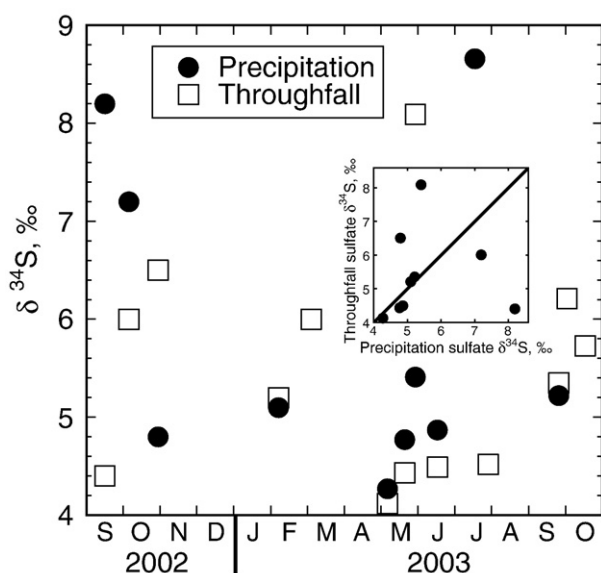

Fig. 1 – Map of Sleepers River W-9 catchment.

Fig. 2 – Sulfate δ^{34}S values in precipitation and throughfall for Water Year 2003 at the Sleepers River W-9 catchment. Inset shows comparison of values for the 9 common collection periods; Line is a 1:1 line.

under a mature *A. saccharum* (sugar maple), the dominant tree species in the catchment. Collection intervals were irregular but approximately monthly, and samples represented all precipitation between collections. During the latter part of the growing season (July to October), we sampled precipitation in the same manner but we sampled throughfall by an alternate method. On 4 occasions, we collected 3 weekly throughfall samples, each of which was pooled from eight 20-cm funnel collectors within a specific forest type. These 3 samples represented the diversity of canopy species in the catchment. During Water Year 2003, stream samples from the W-9 outlet were collected manually every week, and with automatic samplers triggered by a rise in stage during selected high-flow events. Several stream samples were also collected during the 2004 snowmelt, mostly at high flow.

An aliquot of each sample was filtered (0.45 μm) and shipped on ice to a laboratory at the State University of New York, College of Environmental Science and Forestry for analysis of anions by ion chromatography (IC) and cations by inductively coupled plasma emission spectrophotometry (ICP). For isotope analyses, 10 l (precipitation and throughfall) or 1 l (stream) samples were dripped through anion exchange resin columns to collect the sulfate. Resin columns were sent to the Isotope Science Laboratory (ISL) at the University of Calgary (Alberta, Canada), where sulfate was eluted from the column and precipitated as $BaSO_4$ by adding a $BaCl_2$ solution. The $BaSO_4$ was filtered, washed and dried, then converted in an elemental analyzer to SO_2, which was swept with a He stream into an isotope ratio mass spectrometer (VG Prism II) for isotope ratio determinations. Stable isotope ratios are reported in the usual δ notation in per mil with respect to the international standard V-CDT for S isotope measurements. Precision (standard deviation on replicate analyses) averaged ±0.26‰ for δ^{34}S values.

3. Results

3.1. Precipitation and throughfall

The δ^{34}S values of precipitation sulfate ($n=10$) ranged from 4.3 to 8.7‰ (Fig. 2), with an average of 5.9±1.6‰. All but three of the values were between 4.3 and 5.4‰.The δ^{34}S values of throughfall sulfate ($n=13$) ranged from 4.1 to 8.1‰, with an average of 5.5±1.1‰. Only one value exceeded 6.5‰. Despite the similarity in ranges and means of precipitation and throughfall δ^{34}S, corresponding values from common collection periods ($n=9$) were often quite different (Fig. 2). Five of the paired values differed by less than 0.4‰, but the other four pairs differed by 1.2 to 3.5‰. Among the latter, the δ^{34}S values of throughfall sulfate were higher in two cases and lower in the other two cases than δ^{34}S values of precipitation. No seasonal pattern in δ^{34}S values was apparent for either precipitation or throughfall. For the period in which throughfall was obtained from the distributed collectors, δ^{34}S values among the three plots were similar, with a standard deviation of 0.6‰ or less for all four dates (Table 1).

3.2. Surface water: 2003 water year

δ^{34}S values in weekly stream water sulfate samples followed a distinct seasonal pattern, decreasing from nearly 8‰ in early fall to 6.5‰ in winter, reaching a minimum of 6.2‰ during snowmelt, then increasing through the spring and summer to a peak of 10.3‰ near the end of summer (Fig. 3). δ^{34}S values then returned to values in the 8 to 9‰ range, similar to the start of the water year. For several months in summer and fall, stream δ^{34}S values exceeded 8‰, the value previously used for the bedrock weathering end member based on winter base flow conditions (Shanley et al., 2005). Storm-flow samples and weekly samples that coincided with high flow had δ^{34}S values that deviated from the smooth seasonal pattern.

Streamwater sulfate sampled during storms consistently had lower δ^{34}S values, typically deviating 1 to 3‰, and as much as 5‰ during two storms in September 2002, from the general seasonal pattern (Fig. 3). In the September 2002 storms, δ^{34}S values decreased below 5.6‰, the value previously used as the precipitation end member (Shanley et al., 2005). This 1 to 5‰ range in δ^{34}S values of streamwater sulfate within individual storms exceeded the range during the entire 2000 snow melt. The overall range in δ^{34}S values of streamwater sulfate for the water year was 6.4‰ (4.0 to 10.4‰), with much greater temporal variability compared to our earlier snowmelt study (Shanley et al., 2005).

Table 1 – Average throughfall sulfate δ^{34}S-values and standard deviations for collections made from 3 plots on each sampling date

Date	δ^{34}S	Std. dev.
7/28/03	4.52	0.48
9/24/03	5.35	0.13
10/1/03	6.21	0.36
10/16/03	5.73	0.61

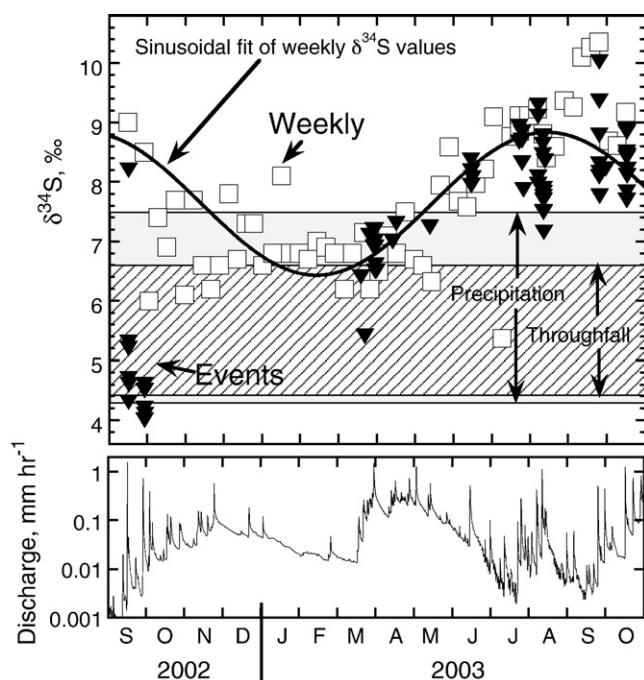**Fig. 3 – Hydrograph and δ^{34}S values of streamwater sulfate at Sleepers River W-9 for Water Year 2003, including weekly and event samples. The range (+/– one standard deviation of the mean) of δ^{34}S values of sulfate in precipitation and throughfall are shown.**

3.3. Storm of 15 September 2002

Following 7 weeks of well below average precipitation, an intense convective storm on 15 September 2002 deposited 51 mm rain in 1 h, causing a sharp peak in discharge (Fig. 4). Sulfate concentrations varied inversely with discharge and were diluted by nearly 50% at peak flow compared to pre-storm values. The δ^{34}S value of streamwater sulfate at base flow prior to the storm was 9.0‰. Stream sulfate δ^{34}S values decreased rapidly to 5.3‰ with the initial hydrograph rise, then continued to decrease more gradually to 4.5‰ through the hydrograph peak and well into the recession limb of the hydrograph. At 2 h after peak flow, when discharge had receded to 10% of the storm peak, sulfate concentration had nearly returned to its pre-storm value, but the stream sulfate δ^{34}S value remained low at 4.6‰. Nitrate and DOC concentrations (not shown) increased several fold and peaked slightly after the hydrograph peak. Nitrate concentrations remained high through the recession. Similarly to sulfate, base cation concentrations (not shown) decreased with increasing flow but returned more gradually to pre-storm concentrations than sulfate (Fig. 4).

3.4. Snowmelt in 2003 and 2004

The 2003 and 2004 snowmelt periods had considerably less runoff than the 2000 snowmelt (Shanley et al., 2005). The 2003 snowmelt had one large peak of 1.3 mm h^{-1}, similar to the 2000 peak, whereas the 2004 snowmelt was prolonged but flow never exceeded 0.5 mm h^{-1} (Fig. 5). In 2000, stream sulfate δ^{34}S

values decreased from 8.0‰ prior to melt to 6.8‰ at peak snowmelt, which represented a shift from a predominantly bedrock-derived sulfate source to an approximately equal mixture of bedrock and atmospheric/pedogenic sources. During the 2003 melt peak, δ^{34}S values decreased from 7.2 to 6.5‰, though some greater decreases occurred during two earlier small peaks (Fig. 5). During the 2004 melt, stream sulfate δ^{34}S values decreased only from 7.4 to 7.1‰, remaining virtually constant within the analytical uncertainty. In contrast to the muted isotopic response, sulfate concentration decreased from 180 to 105 µeq l^{-1} in 2004, only slightly less than the 50% dilution for the other two snowmelt periods.

4. Discussion

Precipitation and throughfall sulfate each had similar ranges of δ^{34}S values, with the mean only slightly higher (by 0.4‰) for precipitation, consistent with other studies reporting minimal differences. Novak et al. (2001) reported about 1‰ lower δ^{34}S in throughfall sulfate compared to precipitation, whereas Zhang et al. (1998) reported δ^{34}S values of throughfall that were slightly higher than precipitation in summer and slightly lower than precipitation in winter. The discrepancies between δ^{34}S in throughfall and precipitation sulfate (as much as 3.5‰; Fig. 2) on some sampling dates were enigmatic. The few δ^{34}S values higher than 7‰ were still within the range of up to 8‰ reported at Hubbard Brook, NH (Zhang et al., 1998) or 9‰ reported at an Ontario, Canada site (Hesslein et al., 1988), and may indicate slightly elevated contributions of marine sulfate in these precipitation events. In general, our results are in agreement with other measurements of δ^{34}S values of precipitation sulfate in this region (Alewell et al., 2000; Wadleigh et al., 1996), and tend to validate our atmospheric
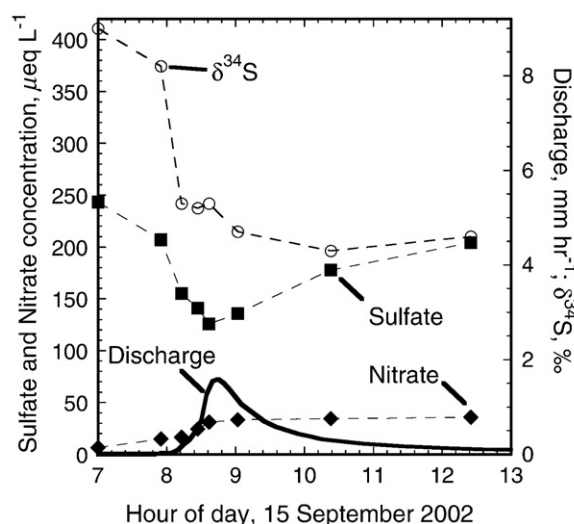

Fig. 4 – Stream sulfate and nitrate concentrations and sulfur isotopic response to intense 51-mm rain event on 15 September 2002. The first sample shown was actually collected on the prior evening under similar base flow conditions.
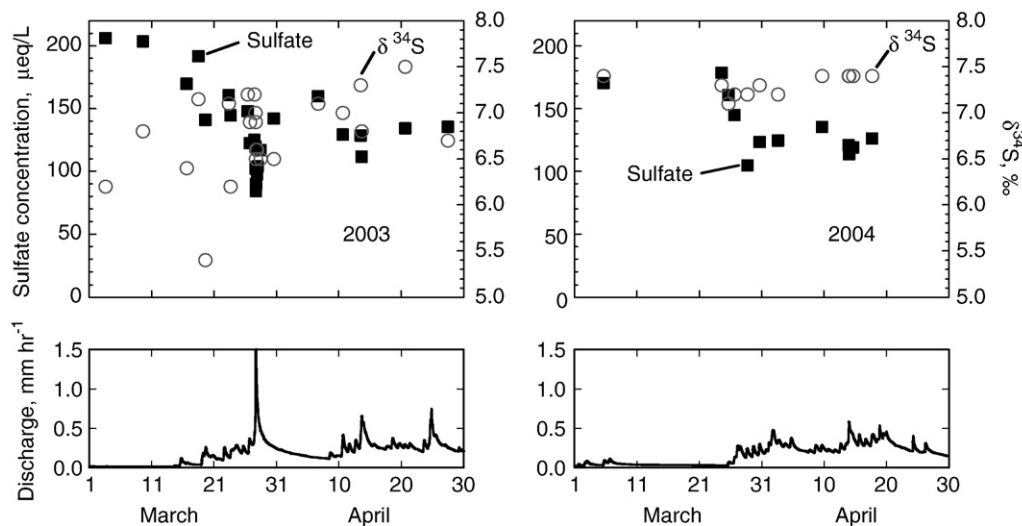
Fig. 5 – Stream hydrographs, sulfate concentrations, and $\delta^{34}S$ values of sulfate during the 2003 and 2004 snowmelt events.

end member $\delta^{34}S$ value of 5.6‰ that was derived from snowpack samples but applied to atmospheric S in general (Shanley et al., 2005). Furthermore, the generally close agreement of mean precipitation and throughfall $\delta^{34}S$ values suggests that the measurement of $\delta^{34}S$ of sulfate in open precipitation is adequate to characterize sulfate isotopic inputs to the forest floor.

The sinusoidal annual pattern of $\delta^{34}S$ values of streamwater sulfate (Fig. 3) cannot be explained by variations of $\delta^{34}S$ values in precipitation, because the latter have a smaller $\delta^{34}S$ range than streamwater and lack a seasonal pattern. The sinusoidal pattern is also not likely caused by variations in $\delta^{34}S$ values of bedrock minerals (e.g., sulfides), as the stream tends to integrate sulfate contributions from the watershed (Likens and Bormann, 1995). The most plausible explanation is that both the annual pattern in the $\delta^{34}S$ values of streamwater sulfate as well as the short-term response to high-flow events is controlled by shifting proportions of lithogenic and pedogenic sulfate, which have different $\delta^{34}S$ values in this watershed. Dissimilatory bacterial sulfate reduction (BSR) may cause additional variation of $\delta^{34}S$ values of streamwater sulfate (Eimers et al., 2004; Mitchell et al., 2006, in press).

During the fall, rising water tables flush soil water to the stream, causing an increase in the contribution of pedogenic sulfate, which has $\delta^{34}S$ values of 5 to 6‰ because its S is derived from the atmosphere and undergoes little isotopic fractionation during uptake, immobilization, and subsequent mineralization (Shanley et al., 2005). Increased pedogenic sulfate contributions are responsible for decreasing the base flow $\delta^{34}S$ values of streamwater sulfate from near 9‰ in the fall to between 6 and 7‰ in winter (Fig. 3). Winter base flow $\delta^{34}S$ values were notably lower prior to the 2003 and 2004 snowmelts compared to the 8‰ previously used as the bedrock value during the 2000 snowmelt (Fig. 5). During snowmelt, soil water sulfate and possibly direct atmospheric sulfate caused a dilution of stream sulfate and a slight decrease in its $\delta^{34}S$ values, but thereafter the increasing dominance of groundwater caused stream sulfate concentrations and $\delta^{34}S$ values to increase steadily throughout the summer months. The decreases in $\delta^{34}S$ values that occurred

during snowmelt and rain storms resulted from inputs of pedogenic and atmospheric sulfate isotopically depleted in ^{34}S relative to the sulfate in groundwater that supplied base flow.

The $\delta^{34}S$ values of streamwater sulfate of >10‰ are notably higher than the previously determined weathering end member value of 8.0‰ (Shanley et al., 2005) and the value of 8.5‰ previously reported for total S in Sleepers River bedrock (Bailey et al., 2004). More extensive recent measurements suggest a higher $\delta^{34}S$ value for bedrock-derived sulfate. Bedrock units with elevated total S contents between 600 and 13,000 mg kg^{-1} were all characterized by elevated $\delta^{34}S$ values between 6 and 14‰. The S-content weighted average $\delta^{34}S$ value of total S in bedrock was 10.3‰ ($n = 14$), virtually equal to the maximum values observed in streamwater sulfate. The $\delta^{34}S$ values of streamwater sulfate progressively increased in summer and early fall as bedrock-derived sulfate increasingly dominated and pedogenic sulfate contributions gradually diminished.

Dissimilatory BSR would also tend to increase $\delta^{34}S$ values of streamwater sulfate in summer and early fall. As sulfate is reduced in anoxic stream sediments and riparian soils, the produced sulfide is depleted in ^{34}S and the remaining sulfate becomes progressively enriched in ^{34}S (Krouse and Mayer, 2000). Removal of sulfate by this process would tend to lower sulfate concentrations in streamwater. Instead, sulfate concentrations consistently increased throughout the summer and were highest during late summer and early fall (Fig. 3) when dissimilatory BSR effects would be expected to peak. However, seasonal variations in the relation between stream sulfate concentration and discharge (Fig. 6A) suggest an influence of dissimilatory BSR.

In winter and spring, stream sulfate concentration had a strong log-linear relation ($r^2 = 0.97$) to stream discharge (Fig. 6A), suggesting simple two-source mixing between lithogenic and pedogenic sulfate. During these seasons, low temperatures should minimize any effect of dissimilatory BSR on $\delta^{34}S$ values of streamwater sulfate. The summer points all plot below this line, i.e. for a given discharge the sulfate concentration is lower, suggesting removal by dissimilatory
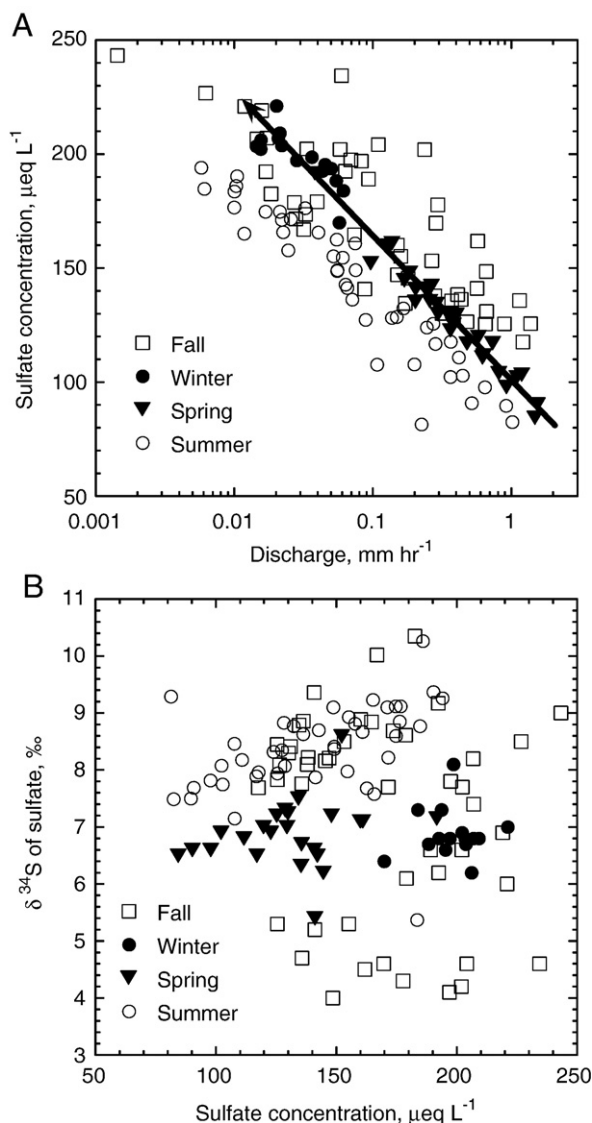
Fig. 6 – Seasonal relations of (A) stream sulfate concentrations to stream discharge and (B) δ^{34}S values to concentration of streamwater sulfate. Seasons were based on hydrologic shifts and accordingly were adjusted slightly from calendar dates (by no more than 10 days).

BSR (although in-stream uptake by biota cannot be ruled out). The fall points plot on either side of the winter/spring line. Fall points below the line reflect continued BSR from summer into early fall, whereas fall points above the line reflect release of sulfate derived from reoxidation of the product sulfides and/or release of accumulated pedogenic sulfate by rising water tables and fall flushing events (Fig. 6A).

Seasonal variations in the relation of δ^{34}S values versus concentrations of sulfate in streamwater (Fig. 6B) provide additional insights. The positive relation in summer is consistent with increasing lithogenic sulfate contributions throughout the summer as flow decreases while streamwater sulfate concentration increases. Some of the fall points coincide with this trend, but the wide scatter in the relation during fall, especially the relatively high concentrations of

sulfate coinciding with low δ^{34}S values, is strong evidence for release during storms of sulfate derived from reoxidation of secondary sulfides. Note the narrow range of δ^{34}S values in winter and spring. Winter sulfate concentrations overlap or exceed the highest summer sulfate concentrations, but with considerably lower δ^{34}S values of sulfate. A possible explanation is that summer and early fall is the most important time for the oxidation of sulfides in the bedrock as a result of low water tables.

The 1 to 3‰ decrease in δ^{34}S values of streamwater sulfate during storm events (Fig. 3) can generally be explained by inputs of pedogenic sulfate. But during the 15 and 27 September 2002 events, δ^{34}S values of streamwater sulfate decreased by ~5‰, to values significantly lower than δ^{34}S values of atmospheric/ pedogenic sulfate (Figs. 3, 4). The isotopic patterns during these events likely reflect some input of ^{34}S-depleted sulfate derived from reoxidation of secondary sulfides. Following drought conditions and/or in watersheds with extensive wetlands, rewetting can release large quantities of sulfate produced from the reoxidation of secondary sulfides as water tables fall and soils become aerobic (Warren et al., 2001; Eimers and Dillon, 2002; Schiff et al., 2005; Mitchell et al., 2006, in press). Inter-annual variations in the extent of dissimilatory BSR and reoxidation may explain the different pre-melt δ^{34}S values of streamwater sulfate in 2003 and 2004 compared to 2000, suggesting caution in assigning baseflow δ^{34}S values to the lithogenic source end member.

While dissimilatory BSR and reoxidation of the product sulfides appear to affect stream sulfate concentrations at Sleepers River at times, weathering of sulfides in bedrock is a more fundamental control on streamwater sulfate dynamics at this site. We emphasize this point because net sulfate export from a catchment is sometimes attributed to net mineralization of organic S or net sulfate desorption without first ruling out a lithogenic source. Despite relatively high atmospheric deposition of sulfate (7.2 kg ha^{-1}yr^{-1} as S), bedrock weathering supplies more than half of the annual sulfate export at Sleepers River (17.1 kg ha^{-1}yr^{-1} as S; Hornbeck et al., 1997). Even during events in which isotopic evidence suggests that sulfate formed from reoxidized secondary sulfides is flushed to streamwater, sulfate still dilutes with flow (Figs. 3, 4, 6). Mitchell et al. (in press) compared some of the fall storms in the current study to those at two other northeastern U.S. sites. During fall storms at the Archer Creek watershed in the Adirondack Mountains, New York, sulfate concentration increased with increasing flow, showing a greater importance of sulfate release from reoxidation of secondary sulfides at that site. However, even for this watershed, sulfate isotope evidence also suggested a potential bedrock weathering source (Campbell et al., 2006).

5.   Conclusions

The δ^{34}S values of streamwater sulfate at Sleepers River, Vermont varied dynamically over an annual cycle with a much greater range (4.0 to 10.4‰) than previously observed during snowmelt (6.8 to 8.0‰). As in the earlier snowmelt study, lithogenic sulfate dominated in streamwater, but δ^{34}S values decreased by 1 to 3‰ during high flows due to mixing

with more ^{34}S-depleted pedogenic sulfate. Mixing of sulfate from lithogenic and pedogenic sources is the primary control on sulfate concentrations and δ^{34}S values in streamwater at this site. The δ^{34}S values of stream sulfate exceeding 10‰ in summer and fall suggest that the lithogenic end member value is higher than indicated in the earlier study, though there may be some influence of dissimilatory bacterial sulfate reduction. Reoxidation of the resulting secondary sulfides and flushing during late summer and fall storms caused decreases in the δ^{34}S values of stream sulfate to below atmospheric values. This study demonstrates that careful analysis of frequently obtained hydrological, chemical, and isotopic data can yield refined insights into S cycling in watersheds.

Acknowledgments

REFERENCES

Alewell C, Mitchell MJ, Likens GE, Krouse HR. Sources of stream sulfate at the Hubbard Brook Experimental Forest: long-term analyses using stable isotopes. Biogeochem 1999;44:281–99.

Alewell C, Mitchell MJ, Likens GE, Krouse HR. Assessing the origin of sulfate deposition at the Hubbard Brook Experimental Forest. J Environ Qual 2000;29:759–67.

Bailey SW, Mayer B, Mitchell MJ. The influence of mineral weathering on drainage water sulfate in Vermont and New Hampshire. Hydrol Proc 2004;18:1639–53. doi:10.1002/hyp.1410.

Campbell J, Mitchell MJ, Mayer B. Isotopic assessment of NO_3^- and SO_4^{2-} mobility during winter in two adjacent watersheds in the Adirondack Mountains, New York. J Geophys Res 2006;111:G04007. doi:10.1029/2006JG000208.

Driscoll CT, Likens GE, Church MR. Recovery of Surface waters in the Northeastern U.S from decreases in the atmospheric deposition of sulfur. Water Air Soil Pollut 1998;105:319–29.

Eimers MC, Dillon PJ. Climate effects on sulphate flux from forested catchments in south-central Ontario. Biogeochem 2002;61:337–55.

Eimers MC, Dillon PJ, Schiff SL. A S-isotope approach to determine the relative contribution of redox processes to net SO4 export from upland and wetland-dominated catchments. Geochim Cosmochim Acta 2004;68:3665–74.

Hall LM. The geology of the St. Johnsbury Quadrangle, Vermont and New Hampshire. Bulletin No. 13. Montpelier: Vermont Development Commission; 1959. 105 pp.

Hesslein RH, Capel MJ, Fox DE. Sulfur isotopes in sulfate in the inputs and outputs of a Canadian Shield watershed. Biogeochem 1988;5:263–73.

Hornbeck JW, Bailey SW, Buso DC, Shanley JB. Streamwater chemistry and nutrient budgets for forested watersheds in New England: variability and management implications. For Ecol Manag 1997;93:73–89.

Huntington TG, Hooper RP, Aulenbach BT. Hydrologic processes controlling sulfate mobility in a small forested watershed. Water Resour Res 1994;30:283–95.

Krouse HR, Mayer B. Sulphur and oxygen isotopes in sulphate. In: Cook P, Herczeg AL, editors. Environmental tracers in subsurface hydrology. Kluwer Academic Publishers; 2000. p. 195–231.

Likens GE, Bormann FH. Biogeochemistry of a forested ecosystem. New York: Springer-Verlag; 1995. 159 pp.

Likens GE, Driscoll CT, Buso DC, Mitchell MJ, Lovett GM, Bailey SW. The biogeochemistry of sulfur at Hubbard Brook. Biogeochem 2002;60:235–316.

Mayer B, Fritz P, Prietzel J, Krouse HR. The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. Appl Geochem 1995;10:161–73.

Mayer B, Prietzel J, Krouse HR. The influence of sulfur deposition rates on sulfate retention patterns and mechanisms in aerated forest soils. Appl Geochem 2001;16:1003–19.

Mitchell MJ, Alewell C. Sulfur transformations and fluxes. In: Chesworth W, editor. The Encyclopedia of Soil Science. Dordrecht: Springer-Verlag; 2007. p. 757–64.

Mitchell MJ, David MB, Maynard DG, Telang SA. Sulfur constituents in soils and streams of a watershed in the Rocky Mountains of Alberta. Can J For Res 1986;16:315–20.

Mitchell MJ, Piatek KB, Christopher SF, Mayer B, Kendall C, McHale PJ. Solute sources in stream water during consecutive fall storms in a northern hardwood forest watershed: a combined hydrological, chemical and isotopic approach. Biogeochem 2006;78:217–46.

Mitchell MJ, Bailey SW, Shanley JB, Mayer B. Evaluating storm events for three watersheds in the northeastern United States: a combined hydrological, chemical and isotopic approach. Hydrol Proc in press.

Nodvin SC, Driscoll CT, Likens GE. Effect of pH on sulfate adsorption by a forest soil. Soil Sci 1986;142:69–75.

Novak M, Bottrell SH, Prechova E. Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living Sphagnum along a NW–SE transect across Europe. Biogeochem 2001;53:23–50.

Park J, Mitchell MJ, McHale PJ, Christopher SF, Myers TP. Interactive effects of changing climate and atmospheric deposition on N and S biogeochemistry in a forested watershed of the Adirondack Mountains, New York State. Glob Change Biol 2003;9:1602–19.

Rochelle BP, Church MR, David MB. Sulfur retention at intensively studies sites in the U.S. and Canada. Water Air Soil Pollut 1987;33:73–83.

Schiff SL, Spoelstra J, Semkin RG, Jeffries DS. Drought induced pulses of SO_4^{2-} from a Canadian shield wetland: use of δ^{34}S and δ^{18}O in SO_4^{2-} to determine sources of sulfur. Appl Geochem 2005;20:691–700.

Shanley JB, Peters NE. Variations in aqueous sulfate concentrations at Panola Mountain, Georgia. J Hydrol 1993;146:361–82.

Shanley JB, Krám P, Hruška J, Bullen TD. A biogeochemical comparison of two well-buffered catchments with contrasting histories of acid deposition. Water Air Soil Pollut Focus 2004;4:325–42.

Shanley JB, Mayer B, Mitchell MJ, Michel RL, Bailey SW, Kendall C. Tracing sources of streamwater sulfate during snowmelt using S and O isotope ratios of sulfate and ^{35}S activity. Biogeochem 2005;76:161–85.

Swank WT, Fitzgerald JW, Ash JT. Microbial transformation of sulfate in forest soils. Science 1984;223:182–4.

Wadleigh MA, Schwarcz HP, Kramer JR. Isotopic evidence for the origin of sulphate in coastal rain. Tellus 1996;48B:44–59.

Warren FJ, Waddington JM, Bourbonniere RA, Day SM. Effect of drought on hydrology and sulphate dynamics in a temperate swamp. Hydrol Proc 2001;15:3133–50.

Zhang Y, Mitchell MJ, Christ M, Likens GE, Krouse HR. Stable sulfur isotopic biogeochemistry of the Hubbard Brook Experimental Forest, New Hampshire. Biogeochem 1998;41:259–75.